ACS OMEGA

Article

Cite This: ACS Omega 2018, 3, 13081−13088

http://pubs.acs.org/journal/acsodf

Mild, Efficient, and Metal-Free Radical 1,2-Dithiocyanation of Alkynes and Alkenes at Room Temperature

Satyajit Samanta,[†] Rana Chatterjee,[†] Sougata Santra,[‡] Alakananda Hajra,[†] Igor A. Khalymbadzha,[‡] Grigory V. Zyryanov,[‡,§] and Adinath Majee*[,†]

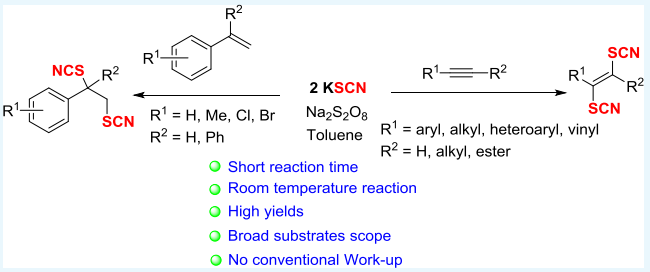
[†]Department of Chemistry, Visva-Bharati (A Central University), Santiniketan 731235, India

[‡]Department of Organic & Biomolecular Chemistry, Chemical Engineering Institute, Ural Federal University, 19 Mira Str., Yekaterinburg 620002, Russian Federation

[§]I. Ya. Postovskiy Institute of Organic Synthesis, Ural Division of the Russian Academy of Sciences, 22 S. Kovalevskoy Str., Yekaterinburg 620219, Russian Federation

Supporting Information

ABSTRACT: A transition metal-free process has been reported for 1,2-dithiocyanation of alkynes in the presence of sodium persulfate and potassium thiocyanate reagent combination in a short reaction time under ambient air. Styrene derivatives are equally applicable under the same reaction conditions. Monothiocyanated vinyl derivatives were also synthesized from 2-ethynylpyridine and dimethyl acetylene dicarboxylate. The reaction proceeds by the radical/polar pathway as evidenced from our experiments and literature. After removal of the solvent from the reaction mixture by evaporation, the crude product was purified without conventional workup.

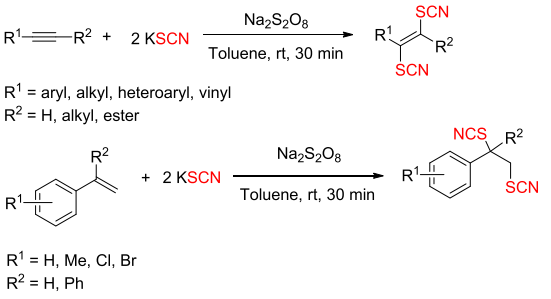


INTRODUCTION

Difunctionalization of organic substrates is a powerful tool in modern organic synthesis, which mainly involves alkynes as well as alkenes in organic synthesis.[1−13] It has been widely studied and utilized in various techniques for functional group interconversions.[14−17] Difunctionalization of alkenes is an attractive method for introducing a set of groups during a one-pot reaction process.[18,19] Dithiocyanation of alkynes and alkenes is meaningful as they show fungicidal activity.[20] In addition, different sulfur derivatives can be synthesized from the thiocyanates.[21−24] These can be easily converted to different compounds such as sulfides, disulfides, thioesters, thiols, thiocarbamates, and many sulfur heterocycles.[25−34] Therefore, efficient incorporation of the thiocyano group into organic molecules has drawn much attention.

Few methods have been developed for the dithiocyanation of alkenes using different catalytic systems such as combination of $PhI(OAc)_2$/trialkylsilyl cyanide or potassium thiocyanate (KSCN) reagent,[35,36] cerium(IV) ammonium nitrate-mediated thiocyanation of styrenes,[37] $FeCl_3$,[38] and recently Cu-catalyzed dithiocyanation in the presence of NH_4SCN and selectfluor reagent combination.[39] However, to the best of our knowledge, dithiocyanation of alkynes is very rare. Only one method has been reported previously.[40] It is worthy to mention that most of the previous methods suffer from at least one of the following general disadvantages such as low-to-moderate yields, lengthy reaction time, vigorous conditions, use of toxic as well as expensive metals, and complex reagent combination. It should be mentioned that none of these methods are applicable for dithiocyanation of both alkynes and alkenes under fully similar conditions. Hence, the development of a new and common reagent system which is useful for synthesizing dithiocyanate derivatives from alkynes as well as alkenes is highly desirable. Therefore, in continuation of our research,[41−47] herein we are pleased to report a simple and convenient process for the dithiocyanation of alkynes as well as alkenes in a short reaction time in the presence of potassium thiocyanate and sodium persulfate reagent combination (Scheme 1).

Scheme 1. Transition Metal-Free 1,2-Dithiocyanation of Alkynes and Alkenes



Received: July 24, 2018
Accepted: September 28, 2018
Published: October 11, 2018

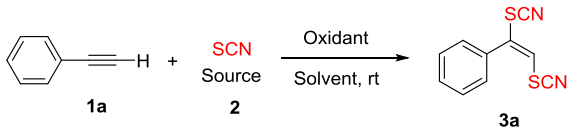
DOI: 10.1021/acsomega.8b01762
ACS Omega 2018, 3, 13081−13088

RESULTS AND DISCUSSION

This study was initiated by observing the reaction of 1 equiv of phenyl acetylene **1a** and 2 equiv of KSCN (**2**) employing 1 equiv of sodium persulfate ($Na_2S_2O_8$) as the oxidant in 1,2-dichloroethane (1,2-DCE) solvent at room temperature under ambient air for 30 min. Gratifyingly, the desired dithiocyanated coupling product, (1,2-dithiocyanatovinyl)benzene (**3a**), was obtained in a 55% yield after 30 min (Table 1, entry 1). This result encouraged us to optimize the reaction in different conditions, and the results are summarized in Table 1. To interpret the solvent effects, the reaction was examined in various solvents (Table 1, entries 2−10). To our pleasure, the desired product was isolated in an excellent yield (90%) in toluene after 30 min (Table 1, entry 7). The yield was not improved significantly by increasing the reaction time. Other common solvents such as dichloromethane (DCM), tetrahydrofuran (THF), 1,4-dioxane, CH_3CN, dimethylformamide (DMF), dimethyl sulfoxide (DMSO), poly(ethylene glycol) (PEG)-400, and water were not so effective. Other oxidants such as ammonium persulfate [$(NH_4)_2S_2O_8$], potassium persulfate ($K_2S_2O_8$), and di-*tert*-butyl peroxide (DTBP) were also investigated. These were not so effective for this transformation (Table 1, entries 11−13). Ammonium thiocyanate (NH_4SCN), as the thiocyanate source, is also not effective for this transformation (Table 1, entry 14). A higher amount of oxidant loading (2 equiv) did not improve the yield further (Table 1, entry 15), but on decreasing the amount of oxidant (0.5 equiv), the yield was decreased considerably (Table 1, entry 16). In addition, by increasing the amount of KSCN, the yield was not improved (Table 1, entry 17). The reaction did not proceed at all in the absence of any oxidant (Table 1, entry 18) as well as under neat condition (Table 1, entry 19). Therefore, on the basis of the series of experiments (Table 1, entries 1−19), we considered the optimized reaction conditions by using 2 equiv of KSCN and 1 equiv of $Na_2S_2O_8$ in toluene for 30 min at room temperature under ambient air (Table 1, entry 7).

Considering the optimization of the reaction conditions, we examined the general applicability by increasing the substrate scope (Scheme 2). A series of 1,2-dithiocyanated alkenes were obtained in good to excellent yields under the present reaction conditions (**3a**−**3s**). Phenyl acetylenes with electron-donating substituents on the benzene ring (such as −Me, *tert*-butyl, and −OMe) afforded the corresponding 1,2-dithiocyanated alkenes in excellent yields (**3b**, **3c**, **3d**, and **3e**). Electron-withdrawing substituents on the benzene ring of the phenyl acetylene moiety (such as −F and $-NO_2$) efficiently reacted with KSCN to produce the respective 1,2-dithiocyanated alkene derivatives (**3f**, **3g**, and **3h**). Carbonyl functionality is also well tolerated to afford the desired product in good yield (**3i**). Heteroaryl-substituted terminal alkyne (such as 3-ethynylthiophene **1j**) also reacted smoothly under the optimized reaction conditions (**3j**). In addition, aliphatic terminal alkynes were also found to afford the desired products in high yields (**3k**−**3n**). Apart from

Table 1. Optimization of the Reaction Conditions[a]

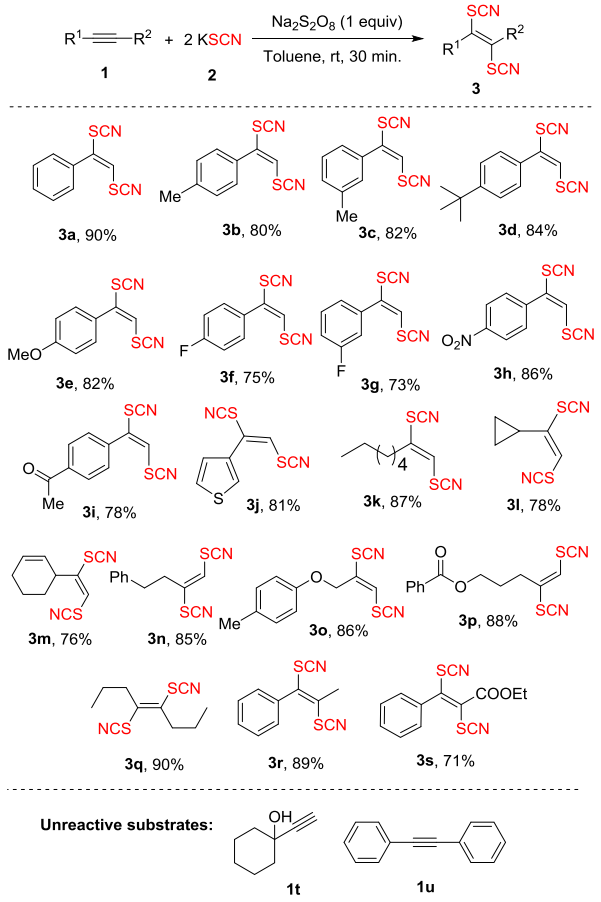


1a 2 3a

entry	source of SCN (equiv)	oxidant (equiv)	solvent (2 mL)	yields (%)[b]
1	KSCN (2)	$Na_2S_2O_8$ (1)	1,2-DCE	55
2	KSCN (2)	$Na_2S_2O_8$ (1)	DCM	85
3	KSCN (2)	$Na_2S_2O_8$ (1)	THF	30
4	KSCN (2)	$Na_2S_2O_8$ (1)	1,4-dioxane	<10
5	KSCN (2)	$Na_2S_2O_8$ (1)	CH_3CN	20
6	KSCN (2)	$Na_2S_2O_8$ (1)	DMF	<10
7	KSCN (2)	$Na_2S_2O_8$ (1)	toluene	90, 92[c]
8	KSCN (2)	$Na_2S_2O_8$ (1)	DMSO	ND
9	KSCN (2)	$Na_2S_2O_8$ (1)	PEG-400	ND
10	KSCN (2)	$Na_2S_2O_8$ (1)	H_2O	ND
11	KSCN (2)	$(NH_4)_2S_2O_8$ (1)	toluene	60
12	KSCN (2)	$K_2S_2O_8$ (1)	toluene	88
13	KSCN (2)	DTBP (1)	toluene	ND
14	NH_4SCN (2)	$Na_2S_2O_8$ (1)	toluene	70
15	KSCN (2)	$Na_2S_2O_8$ (2)	toluene	90
16	KSCN (2)	$Na_2S_2O_8$ (0.5)	toluene	48
17	KSCN (4)	$Na_2S_2O_8$ (1)	toluene	90
18	KSCN (2)		toluene	ND
19	KSCN (2)	$Na_2S_2O_8$ (1)	neat	ND

[a]Reaction conditions: carried out with 1 mmol of **1a** and 2 mmol of SCN source in 2 mL of solvent at room temperature for 30 min. [b]All are isolated yields. [c]Reaction time 12 h.

Scheme 2. Substrate Scope for the 1,2-Dithiocyanation of Various Alkynes[a]



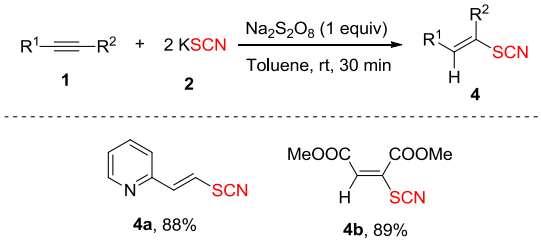
[a]Reaction conditions: **1** (1 mmol) and **2** (2 mmol) in the presence of 1 equiv of $Na_2S_2O_8$ in 2 mL of toluene for 30 min at room temperature.

DOI: 10.1021/acsomega.8b01762
ACS Omega 2018, 3, 13081−13088

aryl acetylenes, alkenyl acetylene (**1m**) is also a good substrate for the reaction. Two oxy-substituted terminal alkynes were also tested; they also furnished the desired products in excellent yields (**3o** and **3p**).

It is worthy to mention that the present reaction conditions are equally effective for internal alkynes. We have examined three different internal alkynes such as oct-4-yne (**1q**), prop-1-yn-1-ylbenzene (**1r**), and ethyl 3-phenylpropiolate (**1s**); all of these afforded the desired products (**3q**−**3s**) in excellent yields. However, 1-ethynylcyclohexan-1-ol (**1t**) and 1,2-diphenylethyne (**1u**) remained unreacted under the present reaction conditions. During our studies on the substrate scope, we have selectively found the 1,2-dithiocyanation product. Only the formation of monothiocyanated alkene derivatives (**4a** and **4b**) has been observed in cases of 2-ethynylpyridine and dimethyl acetylene dicarboxylate in 88 and 89% yields, respectively (Scheme 3).

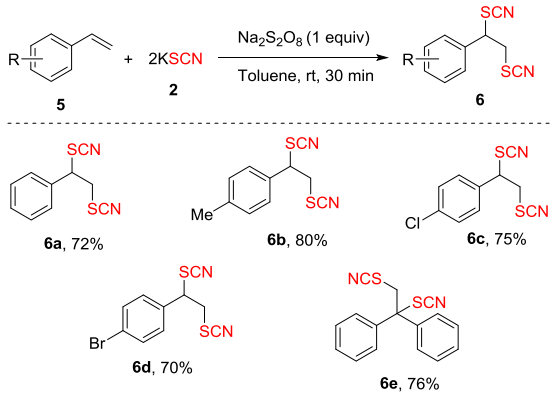
Scheme 3. Formation of Monothiocyanated Vinyl Derivatives[a]



[a]Reaction conditions: **1** (1 mmol) and **2** (2 mmol) in the presence of 1 equiv of $Na_2S_2O_8$ in 2 mL of toluene for 30 min at room temperature.

To explore the scope of the present methodology, we used styrene derivatives to synthesize diverse vicinal dithiocyanate derivatives (Scheme 4). Styrenes **5** with different substituents on the aromatic ring, including electron-donating and electron-withdrawing groups, can be transformed into the corresponding products **6** in good yields. Styrene having a −Me substituent on the benzene ring reacted with KSCN efficiently to afford the product with good yield (**6b**). Halo-substituted

Scheme 4. Synthesis of Diverse Vicinal Dithiocyanate Derivatives from Styrenes[a]

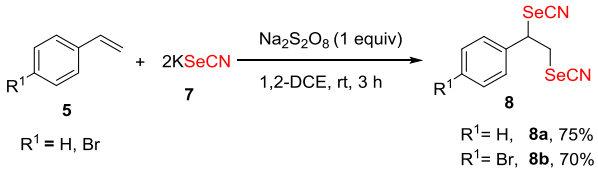


[a]Reaction conditions: 1 mmol of **5** and 2 mmol of **2** in the presence of 1 equiv of $Na_2S_2O_8$ in 2 mL of toluene at room temperature for 30 min.

styrenes were well tolerated in the dithiocyanation reaction (**6c** and **6d**). In addition, we are pleased to notice that 1,1-diphenylethylene (DPE) gave the desired product (**6e**) with good yields under the stated reaction conditions. To make the reaction more greener aspect, we tried the reaction for both alkyne and alkene by light in the presence of a photocatalyst instead of persulfate. The desirable product for alkyne was found with low yield, whereas for styrene no satisfactory product has been isolated (see the Supporting Information).

As an application, we observed that this protocol is extendable for diselenylation of styrenes using KSeCN instead of KSCN with a combination of similar reagents (Scheme 5).

Scheme 5. Diselenylation of Styrenes Using Potassium Selenocyanate[a]



[a]Reaction conditions: **5** (1 mmol) and **7** (2 mmol) in the presence of 1 equiv of $Na_2S_2O_8$ in 2 mL of 1,2-DCE for 3 h at room temperature.

All these reactions are not sensitive to air and moisture and were performed under an open atmosphere. The reaction conditions are mild enough and found no decomposition or polymerization of the starting materials. We have not observed any considerable byproducts for all reactions studied. All of the synthesized compounds have been characterized by spectral data and the new compounds by spectral and analytical data. X-ray crystallographic analysis of ethyl (*E*)-3-phenyl-2,3-dithiocyanatoacrylate (**3s**) was performed to confirm the structure of the product as shown in Figure 1.[48] In addition, we

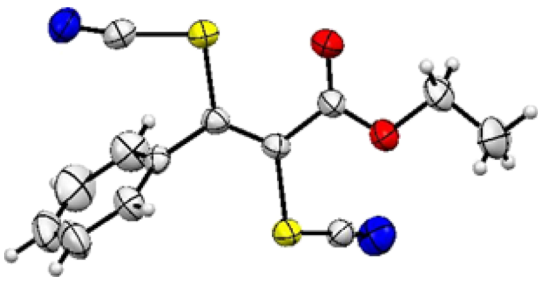


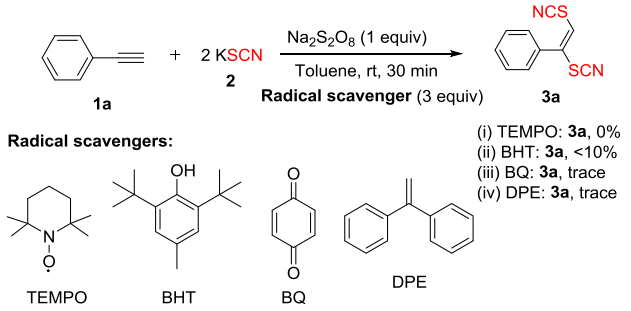
Figure 1. X-ray crystal structure of compound **3s**.

have also carried out correlation spectroscopy and nuclear Overhauser effect NMR experiment of compound **3c** where we did not find any cross-peak and trans-conformation was confirmed. For this present reaction, the workup procedure can be avoided. The solvent (toluene) was evaporated under rotary evaporator after completion of the reaction, and the crude reaction mixture was purified by column chromatography using silica gel.

To get a better understanding of the mechanism of this reaction, few control experiments were carried out (Scheme 6). In the presence of radical scavengers such as (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) and butylated hydroxytoluene (BHT), no product was obtained, whereas a trace amount of product was obtained in the presence of 1,4-

DOI: 10.1021/acsomega.8b01762
ACS Omega 2018, 3, 13081−13088

Scheme 6. Control Experiments[a]



[a]Reaction conditions: **1a** (1 mmol), KSCN (2 mmol), and 3 mmol of different radical scavengers in the presence of 1 equiv of $Na_2S_2O_8$ in 2 mL of toluene for 30 min at room temperature.

benzoquinone (BQ) and DPE. These results suggest that the reaction probably proceeds through a radical pathway.

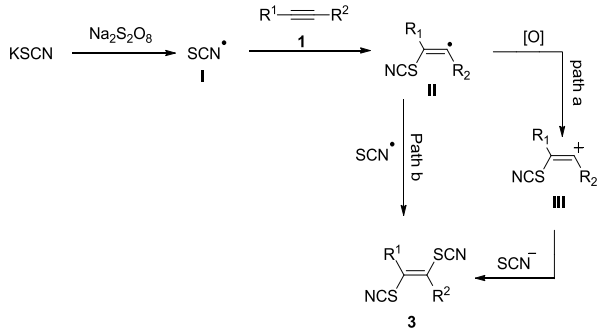
In a mixture (1:1) of phenyl acetylene (**1a**) and DPE (**5e**) with 2 equiv of KSCN when subjected to react under the same reaction conditions, only the DPE (**5e**) participated in the reaction to afford the desired product (**6e**), whereas compound **3a** was isolated as trace amount (Scheme 7). Therefore, the reaction is selective and shows the high reactivity of alkenes than alkynes. In other words, we can say that here DPE (**5e**) acts as a radical scavenger, which also proves that the reaction goes through a radical pathway.

On the basis of the above experimental results and literature,[35−37,49−53] a plausible mechanism is proposed in Scheme 8. Initially, an electrophilic thiocyanate radical I is generated by the oxidation of thiocyanate anion by $Na_2S_2O_8$. Subsequent radical addition of I to alkyne derivative (1) produces carbon-centered radical II, which was further oxidized to the corresponding carbocation III by $Na_2S_2O_8$. Then, the nucleophilic reaction of thiocyanate anion (path a) with the carbocation III forms the desired product **3**. Another pathway is possible (path b), which involves the coupling of thiocyanate radical with intermediate II to form the desired product **3**.

CONCLUSIONS

In summary, we have developed a mild and metal-free method for the 1,2-dithiocyanation of alkynes in a short reaction time using the reagent combination of sodium persulfate and potassium thiocyanate. A variety of 1,2-dithiocyanated alkene derivatives have been synthesized with broad functionalities in high yields. The present methodology is also useful for the dithiocyanation of styrene derivatives to provide a variety of vicinal dithiocyanate derivatives. We also observed the formation of monothiocyanated vinyl derivatives in cases of 2-ethynylpyridine and dimethyl acetylenedicarboxylate. The selectivity of this reaction was also tested by carrying out the reaction between phenyl acetylene and DPE. We believe that our present methodology is a meaningful addition over the existing methods to synthesize important building blocks of 1,2-dithiocyanated alkene and alkane derivatives.

Scheme 8. Proposed Reaction Mechanism



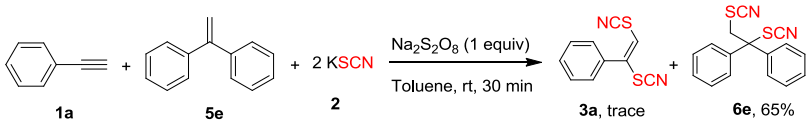
EXPERIMENTAL SECTION

General. All substrates and reagents we have used in the experiment were purchased from commercial sources and used without any purification. ^{1}H NMR spectra were recorded using a 400 MHz spectrometer, and $CDCl_3$ was used as the solvent. Chemical shifts were expressed in parts per million (ppm) (δ) and coupling constants (J) were given in hertz, whereas the signals were represented as s (singlet), d (doublet), t (triplet), m (multiplet), and dd (double doublet). ^{13}C NMR spectra were recorded at 100 MHz, and ^{77}Se NMR spectra were recorded at 76 MHz in $CDCl_3$ solution. Chemical shifts as internal standard were referenced to $CDCl_3$ (δ = 7.26 for ^{1}H and δ = 77.16 for ^{13}C NMR). Precoated silica gel on an aluminum foil was used for thin layer chromatography (TLC) with dried and distilled solvent before use.

General Procedure for the Synthesis of Compounds 3. A mixture of alkyne (**1**, 1 mmol), KSCN (194 mg, 2 mmol), and sodium persulfate (238 mg, 1 mmol) was taken in a dry sealed tube, and 2 mL of toluene was added to this mixture. The resulting mixture was stirred at room temperature for 30 min. After completion of the reaction (TLC), the crude product was isolated just by evaporation of the solvent (toluene) in a rotary evaporator under reduced pressure. No conventional workup procedure has been followed. The crude reaction mixture was purified by column chromatography on silica gel (60−120 mesh) using petroleum ether and ethyl acetate as eluents.

General Procedure for the Synthesis of Compounds 6. A mixture of alkene (**5**, 1 mmol), KSCN (194 mg, 2 mmol), and sodium persulfate (238 mg, 1 mmol) was taken in a dry sealed tube. Toluene (2 mL) was added to the mixture, and the resulting mixture was stirred at room temperature for 30 min. After completion of the reaction (TLC), the solvent (toluene) was evaporated in a rotary evaporator under reduced pressure, and the crude reaction mixture was purified by column chromatography on silica gel (60−120 mesh) using petroleum ether and ethyl acetate as eluents.

Scheme 7. Competitive Reaction between Alkynes and Alkenes



DOI: 10.1021/acsomega.8b01762
ACS Omega 2018, 3, 13081−13088

*(E)-(1,2-Dithiocyanatovinyl)benzene (**3a**).*[40] Colorless solid (196 mg, 90%), mp 63−65 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.52−7.49 (m, 3H), 7.39−7.36 (m, 2H), 6.81 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 131.8, 131.4, 129.7, 128.6, 127.5, 117.2, 108.7, 107.9.

*(E)-1-(1,2-Dithiocyanatovinyl)-4-methylbenzene (**3b**).*[40] Colorless solid (185 mg, 80%), mp 92−94 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.32−7.25 (m, 4H), 6.76 (s, 1H), 2.41 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 142.1, 131.8, 130.4, 128.9, 128.6, 116.3, 109.0, 108.2, 21.7.

*(E)-1-(1,2-Dithiocyanatovinyl)-3-methylbenzene (**3c**).* Light yellow oil (190 mg, 82%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.40−7.36 (m, 1H), 7.34−7.30 (m, 1H), 7.17−7.15 (m, 2H), 6.78 (s, 1H), 2.41 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 139.9, 132.3, 131.7, 129.6, 129.0, 125.8, 116.7, 108.9, 108.1, 21.5. Anal. Calcd for $C_{11}H_8N_2S_2$: C, 56.87; H, 3.47; N, 12.06%. Found: C, 56.77; H, 3.41; N, 12.02%.

*(E)-1-(tert-Butyl)-4-(1,2-dithiocyanatovinyl)benzene (**3d**).* Pale yellow gummy mass (230 mg, 84%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.51−7.47 (m, 2H), 7.31−7.29 (m, 2H), 6.77 (s, 1H), 1.34 (s, 9H): ^{13}C NMR ($CDCl_3$, 100 MHz): δ 155.1, 131.6, 128.8, 128.5, 126.7, 116.3, 109.0, 108.2, 35.2, 31.2. Anal. Calcd for $C_{14}H_{14}N_2S_2$: C, 61.28; H, 5.14; N, 10.21%. Found: C, 61.20; H, 5.21; N, 10.32%.

*(E)-1-(1,2-Dithiocyanatovinyl)-4-methoxybenzene (**3e**).* Pale yellow gummy mass (203 mg, 82%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.33−7.31 (m, 2H), 7.00−6.98 (m, 2H), 6.71 (s, 1H), 3.86 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 161.9, 131.8, 130.4, 123.7, 115.6, 115.1, 109.0, 108.2, 55.6. Anal. Calcd for $C_{11}H_8N_2OS_2$: C, 53.21; H, 3.25; N, 11.28%. Found: C, 53.14; H, 3.13; N, 11.20%.

*(E)-1-(1,2-Dithiocyanatovinyl)-4-fluorobenzene (**3f**).* Pale yellow oil (177 mg, 75%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.41−7.38 (m, 2H), 7.24−7.17 (m, 2H), 6.82 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 164.2 (d, $^1J_{C-F}$ = 253 Hz), 131.0 (d, $^4J_{C-F}$ = 9 Hz), 130.7, 129.8, 127.9, 117.9, 117.2 (d, $^2J_{C-F}$ = 22 Hz), 108.4, 107.7. Anal. Calcd for $C_{10}H_5FN_2S_2$: C, 50.83; H, 2.13; N, 11.86%. Found: C, 50.88; H, 2.06; N, 11.81%.

*(E)-1-(1,2-Dithiocyanatovinyl)-3-fluorobenzene (**3g**).* Yellow oil (172 mg, 73%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.53−7.47 (m, 1H), 7.25−7.16 (m, 2H), 7.14−7.10 (m, 1H), 6.88 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 163.0 (d, $^1J_{C-F}$ = 249 Hz), 133.8, 133.7, 131.7 (d, $^4J_{C-F}$ = 8 Hz), 131.2, 129.8, 126.1, 124.6 (d, $^3J_{C-F}$ = 3 Hz), 119.1, 118.8, 118.6, 115.9 (d, $^2J_{C-F}$ = 23 Hz), 108.3, 107.6. Anal. Calcd for $C_{10}H_5FN_2S_2$: C, 50.83; H, 2.13; N, 11.86%. Found: C, 50.89; H, 2.04; N, 11.80%.

*(E)-1-(1,2-Dithiocyanatovinyl)-4-nitrobenzene (**3h**).* Yellow gummy mass (226 mg, 86%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.40−8.36 (m, 2H), 7.64−7.60 (m, 2H), 7.02 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 138.0, 130.1, 128.4, 125.0, 124.7, 121.5, 107.4, 107.1. Anal. Calcd for $C_{10}H_5N_3O_2S_2$: C, 45.62; H, 1.91; N, 15.96%. Found: C, 45.54; H, 1.82; N, 15.88%.

*(E)-1-(4-(1,2-Dithiocyanatovinyl)phenyl)ethanone (**3i**).* Pale yellow gummy mass (203 mg, 78%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.09−8.06 (m, 2H), 7.52−7.49 (m, 2H), 6.92 (s, 1H), 2.64 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 196.8, 139.1, 136.1, 130.4, 129.6, 129.1, 119.5, 108.1, 107.5, 26.8. Anal. Calcd for $C_{12}H_8N_2OS_2$: C, 55.37; H, 3.10; N, 10.76%. Found: C, 55.30; H, 3.02; N, 10.71%.

*(E)-3-(1,2-Dithiocyanatovinyl)thiophene (**3j**).* Yellow oil (181 mg, 81%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.57−7.56 (m, 1H), 7.51−7.49 (m, 1H), 7.22−7.21 (m, 1H), 6.78 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 132.3, 128.7, 128.4, 126.7, 125.9, 117.3, 108.6, 108.1. Anal. Calcd for $C_8H_4N_2S_3$: C, 42.84; H, 1.80; N, 12.49%. Found: C, 42.74; H, 1.72; N, 12.41%.

*(E)-1,2-Dithiocyanatooct-1-ene (**3k**).* Pale yellow oil (196 mg, 87%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.48 (s, 1H), 2.52 (t, J = 7.6 Hz, 2H), 1.61−1.58 (m, 2H), 1.32−1.31 (m, 6H), 0.91−0.88 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 136.7, 114.3, 108.4, 107.8, 33.1, 31.4, 28.5, 27.4, 22.5, 14.1. Anal. Calcd for $C_{10}H_{14}N_2S_2$: C, 53.06; H, 6.23; N, 12.38%. Found: C, 53.01; H, 6.16; N, 12.30%.

*(E)-(1,2-Dithiocyanatovinyl)cyclopropane (**3l**).* Light yellow oil (142 mg, 78%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.58 (d, J = 1.6 Hz, 1H), 1.77−1.71 (m, 1H), 1.11−1.06 (m, 2H), 0.90−0.86 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 133.8, 117.6, 108.7, 108.4, 14.0, 8.1. Anal. Calcd for $C_7H_6N_2S_2$: C, 46.13; H, 3.32; N, 15.37%. Found: C, 46.07; H, 3.24; N, 15.27%.

*(E)-3-(1,2-Dithiocyanatovinyl)cyclohex-1-ene (**3m**).*[40] Pale yellow liquid (168 mg, 76%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.48 (m, 1H), 5.95−5.93 (m, 1H), 2.23−2.17 (m, 4H), 1.78−1.72 (m, 2H), 1.69−1.64 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 136.5, 133.8, 131.9, 116.9, 109.4, 108.3, 26.5, 25.6, 22.1, 21.3.

*(E)-(3,4-Dithiocyanatobut-3-en-1-yl)benzene (**3n**).* Pale yellow oil (209 mg, 85%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.27−7.17 (m, 3H), 7.10−7.07 (m, 2H), 6.38 (s, 1H), 2.86−2.83 (m, 2H), 2.78−2.74 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 138.2, 134.7, 129.1, 128.9, 128.7, 127.3, 116.7, 108.4, 107.7, 35.2, 33.3. Anal. Calcd for $C_{12}H_{10}N_2S_2$: C, 58.51; H, 4.09; N, 11.37%. Found: C, 58.43; H, 4.02; N, 11.31%.

*(E)-1-((2,3-Dithiocyanatoallyl)oxy)-4-methylbenzene (**3o**).* Yellow solid (225 mg, 86%), mp 50−52 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.16−7.14 (m, 2H), 6.85−6.82 (m, 2H), 6.80 (s, 1H) 4.86 (d, J = 1.2 Hz, 2H), 2.32 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 154.5, 132.5, 130.4, 127.2, 120.9, 114.6, 109.2, 107.8, 67.5, 20.5. Anal. Calcd for $C_{12}H_{10}N_2OS_2$: C, 54.94; H, 3.84; N, 10.68%. Found: C, 54.83; H, 3.80; N, 10.61%.

*(E)-4,5-Dithiocyanatopent-4-en-1-yl benzoate (**3p**).* Pale yellow oil (267 mg, 88%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.05−8.02 (m, 2H), 7.60−7.56 (m, 1H), 7.47−7.43 (m, 2H), 6.55 (s, 1H), 4.35 (t, J = 6.0 Hz, 2H), 2.72 (t, J = 8.0 Hz, 2H), 2.12−2.09 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.3, 134.8, 133.3, 129.7, 129.6, 128.6, 116.4, 107.9, 107.4, 62.9, 29.8, 26.4. Anal. Calcd for $C_{14}H_{12}N_2O_2S_2$: C, 55.24; H, 3.97; N, 9.20%. Found: C, 55.20; H, 3.91; N, 9.12%.

*(E)-4,5-Dithiocyanatooct-4-ene (**3q**).* Colorless solid (203 mg, 90%), mp 53−55 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.71 (t, J = 7.6 Hz, 4H), 1.71−1.65 (m, 4H), 0.99 (t, J = 7.2 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 130.8, 108.4, 37.7, 21.4, 13.4. Anal. Calcd for $C_{10}H_{14}N_2S_2$: C, 53.06; H, 6.23; N, 12.38%. Found: C, 53.01; H, 6.29; N, 12.47%.

*(E)-(1,2-Dithiocyanatoprop-1-en-1-yl)benzene (**3r**).* Yellow oil (206 mg, 89%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.50−7.45 (m, 3H), 7.34−7.28 (m, 2H), 2.61 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 135.0, 130.8, 130.3, 129.5, 129.1, 125.7, 108.6, 108.0, 22.9. Anal. Calcd for $C_{11}H_8N_2S_2$: C, 56.87; H, 3.47; N, 12.06%. Found: C, 56.77; H, 3.40; N, 12.01%.

*(E)-Ethyl 3-Phenyl-2,3-dithiocyanatoacrylate (**3s**).* Colorless solid (206 mg, 71%), mp 104−106 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.51−7.48 (m, 3H), 7.21−7.18 (m, 2H), 4.42−4.37 (m, 2H), 1.39 (t, J = 7.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100

DOI: 10.1021/acsomega.8b01762
ACS Omega 2018, 3, 13081−13088

MHz): δ 163.5, 159.1, 136.1, 131.4, 129.7, 127.4, 113.1, 108.8, 108.7, 64.4, 14.1. Anal. Calcd for $C_{13}H_{10}N_2O_2S_2$: C, 53.78; H, 3.47; N, 9.65%. Found: C, 53.72; H, 3.40; N, 9.57%.

*(E)-2-(2-Thiocyanatovinyl)pyridine (**4a**).* Colorless gummy mass (142 mg, 88%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.61 (d, *J* = 4.8 Hz, 1H), 7.73−7.69 (m, 1H), 7.25−7.23 (m, 1H), 7.20−7.16 (m, 1H), 6.80 (d, *J* = 9.6 Hz, 1H), 6.69 (d, *J* = 9.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 153.9, 147.6, 137.0, 127.0, 123.8, 123.5, 122.2, 115.7. Anal. Calcd for $C_8H_6N_2S$: C, 59.24; H, 3.73; N, 17.27%. Found: C, 59.18; H, 3.82; N, 17.34%.

*Dimethyl 2-Thiocyanatomaleate (**4b**).* Yellow oil (179 mg, 89%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.85 (s, 1H), 3.95 (s, 3H), 3.83 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.0, 161.9, 138.4, 126.2, 108.7, 54.3, 53.1. Anal. Calcd for $C_7H_7NO_4S$: C, 41.79; H, 3.51; N, 6.96%. Found: C, 41.70; H, 3.40; N, 6.87%.

*(1,2-Dithiocyanatoethyl)benzene (**6a**).*[39] White solid (149 mg, 72%); mp 102−104 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.47−7.45 (m, 3H), 7.39−7.36 (m, 2H), 4.67−4.63 (m, 1H), 3.81−3.76 (m, 1H), 3.66−3.60 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 134.2, 130.5, 129.8, 127.7, 110.3, 109.9, 51.6, 38.3.

*1-(1,2-Dithiocyanatoethyl)-4-methylbenzene (**6b**).*[38] White solid, (187 mg, 80%), mp 99−101 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.25 (s, 4H), 4.66−4.62 (m, 1H), 3.80−3.75 (m, 1H), 3.64−3.59 (m, 1H), 2.38 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 140.7, 131.0, 130.4, 127.5, 110.4, 110.1, 51.5, 38.3, 21.4.

*1-Chloro-4-(1,2-dithiocyanatoethyl)benzene (**6c**).*[39] White solid, (191 mg, 75%), mp 88−90 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.45−7.42 (m, 2H), 7.34−7.31 (m, 2H), 4.64−4.60 (m, 1H), 3.78−3.73 (m, 1H), 3.61−3.55 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 136.5, 132.8, 130.1, 129.0, 110.1, 109.6, 50.9, 38.0.

*1-Bromo-4-(1,2-dithiocyanatoethyl)benzene (**6d**).*[39] White solid, (209 mg, 70%), mp 90−92 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.62−7.59 (m, 2H), 7.28−7.25 (m, 2H), 4.62−4.58 (m, 1H), 3.79−3.74 (m, 1H), 3.60−3.54 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 133.3, 133.1, 129.2, 124.8, 110.0, 109.4, 50.9, 38.0.

*(1,2-Dithiocyanatoethane-1,1-diyl)dibenzene (**6e**).* Pale yellow gummy mass (225 mg, 76%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.45−7.37 (m, 6H), 7.34−7.32 (m, 4H), 4.02 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 140.1, 129.2, 129.1, 126.2, 111.3, 72.2, 46.7. Anal. Calcd for $C_{16}H_{12}N_2S_2$: C, 64.84; H, 4.08; N, 9.45%. Found: C, 64.72; H, 4.02; N, 9.35%.

General Procedure for the Synthesis of Compounds 8. A mixture of alkene (**5**, 1 mmol), KSeCN (288 mg, 2 mmol), and sodium persulfate (238 mg, 1 mmol) was taken in a dry sealed tube. 1,2-DCE (2 mL) was added to the mixture, and the resulting mixture was stirred at room temperature for 3 h. After completion of the reaction (TLC), the solvent (1,2-DCE) was evaporated in a rotary evaporator under reduced pressure, and the crude reaction mixture was purified by column chromatography on silica gel (60−120 mesh) using petroleum ether and ethyl acetate as eluents.

*(1,2-Diselenocyanatoethyl)benzene (**8a**).* White solid (235 mg, 75%), mp 105−107 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.45−7.44 (m, 3H), 7.39−7.37 (m, 2H), 5.01−4.97 (m, 1H), 4.05−4.01 (m, 1H), 3.90−3.84 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 134.8, 130.4, 129.9, 127.7, 101.2, 100.0, 48.2, 33.9; ^{77}Se NMR (76 MHz, $CDCl_3$): δ 240.4, 240.2. Anal. Calcd for $C_{10}H_8N_2Se_2$: C, 38.24; H, 2.57; N, 8.92%. Found: C, 38.14; H, 2.51; N, 8.83%.

*1-Bromo-4-(1,2-diselenocyanatoethyl)benzene (**8b**).* White solid (282 mg, 72%), mp 118−120 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.53−7.49 (m, 2H), 7.22−7.18 (m, 2H), 4.87−4.83 (m, 1H), 3.97−3.93 (m, 1H), 3.75−3.69 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 133.1, 132.2, 129.2, 124.6, 100.7, 99.8, 47.4, 33.4; ^{77}Se NMR (76 MHz, $CDCl_3$): δ 245.1, 244.8; Anal. Calcd for $C_{10}H_7BrN_2Se_2$: C, 30.56; H, 1.80; N, 7.13%. Found: C, 30.48; H, 1.73; N, 7.10%.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b01762.

Light-mediated reaction study: photocatalysis reaction of alkyne; structure determination (X-ray crystallographic data for **3s**); and NMR spectra of all the synthesized compounds (PDF).

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: adinath.majee@visva-bharati.ac.in (A.M.).

ORCID

Sougata Santra: 0000-0002-4186-6105

Alakananda Hajra: 0000-0001-6141-0343

Adinath Majee: 0000-0002-5439-6851

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

A.M. acknowledges the financial support from the DST-RSF Major Research Project (ref. no. INT/RUS/RSF/P-08). S.S. and G.V.Z. acknowledge the financial support from the Russian Science Foundation—Russia (ref. # 18-73-00301). The authors are thankful to the DST-FIST and UGC-SAP programme of the Department of Chemistry, Visva-Bharati University.

■ REFERENCES

(1) Zeni, G.; Larock, R. C. Synthesis of Heterocycles via Palladium π-Olefin and π-Alkyne Chemistry. *Chem. Rev.* **2004**, *104*, 2285−2310.

(2) McDonald, R. I.; Liu, G.; Stahl, S. S. Palladium(II)-Catalyzed Alkene Functionalization *via* Nucleopalladation: Stereochemical Pathways and Enantioselective Catalytic Applications. *Chem. Rev.* **2011**, *111*, 2981−3019.

(3) Cardona, F.; Goti, A. Metal-Catalysed 1,2-Diamination Reactions. *Nat. Chem.* **2009**, *1*, 269−275.

(4) Egami, H.; Sodeoka, M. Trifluoromethylation of Alkenes with Concomitant Introduction of Additional Functional Groups. *Angew. Chem., Int. Ed.* **2014**, *53*, 8294−8308.

(5) Chemler, S. R.; Bovino, M. T. Catalytic Aminohalogenation of Alkenes and Alkynes. *ACS Catal.* **2013**, *3*, 1076−1091.

(6) Muñiz, K.; Martínez, C. Development of Intramolecular Vicinal Diamination of Alkenes: From Palladium to Bromine Catalysis. *J. Org. Chem.* **2013**, *78*, 2168−2174.

(7) Huang, S.-X.; Ding, K. Asymmetric Bromoamination of Chalcones with a Privileged N,N′-Dioxide/Scandium(III) Catalyst. *Angew. Chem., Int. Ed.* **2011**, *50*, 7734−7736.

(8) Bataille, C. J. R.; Donohoe, T. J. Osmium-Free Direct *syn*-Dihydroxylation of Alkenes. *Chem. Soc. Rev.* **2011**, *40*, 114−128.

DOI: 10.1021/acsomega.8b01762
ACS Omega 2018, 3, 13081−13088

(9) Chen, D.; Timmons, C.; Wei, H.-X.; Li, G. Direct Electrophilic Diamination of Functionalized Alkenes without the Use of Any Metal Catalysts. *J. Org. Chem.* **2003**, *68*, 5742−5745.
(10) Kolb, H. C.; VanNieuwenhze, M. S.; Sharpless, K. B. Catalytic Asymmetric Dihydroxylation. *Chem. Rev.* **1994**, *94*, 2483−2547.
(11) Zhang, H.; Pu, W.; Xiong, T.; Li, Y.; Zhou, X.; Sun, K.; Liu, Q.; Zhang, Q. Copper-Catalyzed Intermolecular Aminocyanation and Diamination of Alkenes. *Angew. Chem., Int. Ed.* **2013**, *52*, 2529−2533.
(12) Huang, M.-H.; Hao, W.-J.; Li, G.; Tu, S.-J.; Jiang, B. Recent Advances in Radical Transformations of Internal Alkynes. *Chem. Commun.* **2018**, *54*, 10791−10811.
(13) Huang, M.-H.; Hao, W.-J.; Jiang, B. Recent Advances in Radical-Enabled Bicyclization and Annulation/1,*n*-Bifunctionalization Reactions. *Chem.—Asian J.* **2018**, Early View, DOI: 10.1002/asia.201801119.
(14) Block, E.; Schwan, A. L. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1st ed., 1991; Vol. *4*, p. 329.
(15) Minatti, A.; Muñiz, K. Intramolecular aminopalladation of alkenes as a key step to pyrrolidines and related heterocycles. *Chem. Soc. Rev.* **2007**, *36*, 1142−1152.
(16) Jensen, K. H.; Sigman, M. S. Mechanistic Approaches to Palladium-Catalyzed Alkene Difunctionalization Reactions. *Org. Biomol. Chem.* **2008**, *6*, 4083−4088.
(17) Shimizu, Y.; Kanai, M. Recent progress in copper-catalyzed difunctionalization of unactivated carboncarbon multiple bonds. *Tetrahedron Lett.* **2014**, *55*, 3727−3737.
(18) Lan, X.-W.; Wang, N.-X.; Xing, Y. Recent Advances in Radical Difunctionalization of Simple Alkenes. *Eur. J. Org. Chem.* **2017**, *2017*, 5821−5851.
(19) Gao, Y.; Tang, G.; Zhao, Y. Recent Progress toward Organophosphorus Compounds Based on Phosphorus-Centered Radical Difunctionalizations. *Phosphorus, Sulfur Silicon Relat. Elem.* **2017**, *192*, 589−596.
(20) De Mico, A.; Margarita, R.; Mariani, A.; Piancatelli, G. Hypervalent Iodine-Induced Oxidative Nucleophilic Additions to Alkenes: A Novel Acetoxy Thiocyanation Reaction in 1,1,1,3,3,3-Hexafluoropropan-2-ol. *Chem. Commun.* **1997**, *13*, 1237−1238.
(21) Nguyen, T.; Rubinstein, M.; Wakselman, C. Reaction of Perfluoroalkyl Carbanions with Thiocyanates. Synthesis of Fluorinated Sulfides and Sulfenyl Chlorides. *J. Org. Chem.* **1981**, *46*, 1938−1940.
(22) Zhang, Z.; Liebeskind, L. S. Palladium-Catalyzed, Copper(I)-Mediated Coupling of Boronic Acids and Benzylthiocyanate. A Cyanide-Free Cyanation of Boronic Acids. *Org. Lett.* **2006**, *8*, 4331−4333.
(23) Riemschneider, R. Thiocarbamates and Related Compounds. X.1a New Reaction of Thiocyanates. *J. Am. Chem. Soc.* **1956**, *78*, 844−847.
(24) Lee, Y. T.; Choi, S. Y.; Chung, Y. K. Microwave-Assisted Palladium-Catalyzed Regioselective Cyanothiolation of Alkynes with Thiocyanates. *Tetrahedron Lett.* **2007**, *48*, 5673−5677 and references cited therein .
(25) Erian, A. W.; Sherif, S. M. The Chemistry of Thiocyanic Esters. *Tetrahedron* **1999**, *55*, 7957−8024.
(26) Still, I. W. J.; Toste, F. D. Reduction of Aryl Thiocyanates with SmI_2 and Pd-Catalyzed Coupling with Aryl Halides as a Route to Mixed Aryl Sulfides. *J. Org. Chem.* **1996**, *61*, 7677−7680.
(27) Demko, Z. P.; Sharpless, K. B. An Intramolecular [2 + 3] Cycloaddition Route to Fused 5-Heterosubstituted Tetrazoles. *Org. Lett.* **2001**, *3*, 4091−4094.
(28) Laufer, S. A.; Liedtke, A. J. A Concise and Optimized Four-Step Approach toward 2-(Aryl-)alkylsulfanyl-, 4(5)-Aryl-, 5(4)-Heteroaryl-Substituted Imidazoles Using Alkyl- or Arylalkyl Thiocyanates. *Tetrahedron Lett.* **2006**, *47*, 7199−7203.
(29) Garcia, P.; Evanno, Y.; George, P.; Sevrin, M.; Ricci, G.; Malacria, M.; Aubert, C.; Gandon, V. Synthesis of Aminopyridines and Aminopyridones by Cobalt-Catalyzed [2+2+2] Cycloadditions Involving Yne-Ynamides: Scope, Limitations, and Mechanistic Insights. *Chem.—Eur. J.* **2012**, *18*, 4337−4344.
(30) Ke, F.; Qu, Y.; Jiang, Z.; Li, Z.; Wu, D.; Zhou, X. An Efficient Copper-Catalyzed Carbon−Sulfur Bond Formation Protocol in Water. *Org. Lett.* **2011**, *13*, 454−457.
(31) Piekutowska, M.; Pakulski, Z. The Michaelis-Arbuzov rearrangement of anomeric thiocyanates: synthesis and application of S-glycosyl thiophosphates, thiophosphonates and thiophosphinates as glycosyl donors. *Tetrahedron Lett.* **2007**, *48*, 8482−8486.
(32) Patil, A. D.; Freyer, A. J.; Reichwein, R.; Carte, B.; Killmer, L. B.; Faucette, L.; Johnson, R. K.; Faulkner, D. J. Fasicularin, a Novel Tricyclic Alkaloid from the Ascidian Nephteis Fasicularis with Selective Activity against a DNA Repair-Deficient Organism. *Tetrahedron Lett.* **1997**, *38*, 363−364.
(33) Hill, H. A. O. In *Chemistry and Biochemistry of Thiocyanic Acid and Its Derivatives*; Newman, A. A., Ed.; Academic Press: London, 1975;
(34) Dutta, S.; Abe, H.; Aoyagi, S.; Kibayashi, C.; Gates, K. S. DNA Damage by Fasicularin. *J. Am. Chem. Soc.* **2005**, *127*, 15004−15005.
(35) Bruno, M.; Margarita, R.; Parlanti, L.; Piancatelli, G.; Trifoni, M. Hypervalent Iodine Chemistry: Novel and Direct Thiocyanation of Alkenes Using [Bis(acetoxy)iodo]benzene/Trimethylsilyl Isothiocyanate Reagent Combination. Synthesis of 1,2-Dithiocyanates. *Tetrahedron Lett.* **1998**, *39*, 3847−3848.
(36) De Mico, A.; Margarita, R.; Mariani, A.; Piancatelli, G. Radical Additions to Olefins in the Presence of Iodobenzenediacetate: An Easy Route to Alkyl Dithiocyanates. *Tetrahedron Lett.* **1996**, *37*, 1889−1892.
(37) Nair, V.; Nair, L. G. A very efficient cerium (IV) ammonium nitrate (CAN) mediated thiocyanation of aralkenes: Formation of dithiocyanates. *Tetrahedron Lett.* **1998**, *39*, 4585−4586.
(38) Yadav, J.; Reddy, B.; Gupta, M. Ferric(III) Chloride-Promoted Efficient Thiocyanation of Arylalkenes: A Facile Synthesis of Dithiocyanates. *Synthesis* **2004**, *2004*, 1983−1986.
(39) Lv, Y.; Pu, W.; Cui, H.; He, J.; Zhang, Q. Copper-Catalyzed Efficient Dithiocyanation of Styrenes: Synthesis of Dithiocyanates. *Synth. Commun.* **2016**, *46*, 1223−1229.
(40) Prakash, O.; Sharma, V.; Batra, H.; Moriarty, R. M. (Dichloroiodo)benzene and Lead(II) Thiocyanate as an Efficient Reagent Combination for Stereoselective 1,2-Dithiocyanation of Alkynes. *Tetrahedron Lett.* **2001**, *42*, 553−555.
(41) Mahato, S.; Santra, S.; Chatterjee, R.; Zyryanov, G. V.; Hajra, A.; Majee, A. Brønsted acidic ionic liquid-catalyzed tandem reaction: an efficient approach towards regioselective synthesis of pyrano[3,2-c]coumarins under solvent-free conditions bearing lower E-factors. *Green Chem.* **2017**, *19*, 3282−3295.
(42) Kopchuk, D. S.; Chepchugov, N. V.; Kovalev, I. S.; Santra, S.; Rahman, M.; Giri, K.; Zyryanov, G. V.; Majee, A.; Charushin, V. N.; Chupakhin, O. N. Solvent-free synthesis of 5-(aryl/alkyl)amino-1,2,4-triazines and α-arylamino-2,2′-bipyridines with greener prospects. *RSC Adv.* **2017**, *7*, 9610−9619.
(43) Ojha, N. K.; Zyryanov, G. V.; Majee, A.; Charushin, V. N.; Chupakhin, O. N.; Santra, S. Copper Nanoparticles as Inexpensive and Efficient Catalyst: A Valuable Contribution in Organic Synthesis. *Coord. Chem. Rev.* **2017**, *353*, 1−57.
(44) Sarkar, A.; Santra, S.; Kundu, S. K.; Hajra, A.; Zyryanov, G. V.; Chupakhin, O. N.; Charushin, V. N.; Majee, A. A Decade Update on Solvent and Catalyst-Free Neat Organic Reactions: A Step Forward towards Sustainability. *Green Chem.* **2016**, *18*, 4475−4525.
(45) Ghosal, N. C.; Santra, S.; Das, S.; Hajra, A.; Zyryanov, G. V.; Majee, A. Organocatalysis by an Aprotic Imidazolium Zwitterion: Regioselective Ring-Opening of Aziridines and Applicable to Gram Scale Synthesis. *Green Chem.* **2016**, *18*, 565−574.
(46) Santra, S.; Kopchuk, D. S.; Kovalev, I. S.; Zyryanov, G. V.; Majee, A.; Charushin, V. N.; Chupakhin, O. N. Solvent-Free Synthesis of Pillar[6]arenes. *Green Chem.* **2016**, *18*, 423−426.
(47) Kovalev, I. S.; Taniya, O. S.; Slovesnova, N. V.; Kim, G. A.; Santra, S.; Zyryanov, G. V.; Kopchuk, D. S.; Majee, A.; Charushin, V. N.; Chupakhin, O. N. Fluorescent Detection of 2,4-DNT and 2,4,6-

DOI: 10.1021/acsomega.8b01762
ACS Omega 2018, 3, 13081−13088

TNT in Aqueous Media by Using Simple Water-Soluble Pyrene Derivatives. *Chem.−Asian J.* **2016**, *11*, 775−781.
(48) Further information can be found in the CIF file. The crystal data are deposited in the Cambridge Crystallographic Data Centre and assigned as CCDC 1851646.
(49) Nair, V.; George, T. G.; Nair, L. G.; Panicker, S. B. A Direct Synthesis of Aryl Thiocyanates Using Cerium(IV) Ammonium Nitrate. *Tetrahedron Lett.* **1999**, *40*, 1195−1196.
(50) Wu, G.; Liu, Q.; Shen, Y.; Wu, W.; Wu, L. Regioselective Thiocyanation of Aromatic and Heteroaromatic Compounds Using Ammonium Thiocyanate and Oxone. *Tetrahedron Lett.* **2005**, *46*, 5831−5834.
(51) Pan, X.-Q.; Lei, M.-Y.; Zou, J.-P.; Zhang, W. $Mn(OAc)_3$-promoted regioselective free radical thiocyanation of indoles and anilines. *Tetrahedron Lett.* **2009**, *50*, 347−349.
(52) Fan, W.; Yang, Q.; Xu, F.; Li, P. A Visible-Light-Promoted Aerobic Metal-Free C-3 Thiocyanation of Indoles. *J. Org. Chem.* **2014**, *79*, 10588−10592.
(53) Yang, H.; Duan, X.-H.; Zhao, J.-F.; Guo, L.-N. Transition-Metal-Free Tandem Radical Thiocyanooxygenation of Olefinic Amides: A New Route to SCN-Containing Heterocycles. *Org. Lett.* **2015**, *17*, 1998−2001.

DOI: 10.1021/acsomega.8b01762
ACS Omega 2018, 3, 13081−13088